NEUTRON SCATTERING STUDIES OF FUNDAMENTAL PROCESSES IN EARTH MATERIALS

Final Report
For Period July 15, 2001 – July 14, 2005

K. R. McCall

Department of Physics
University of Nevada
Reno, Nevada 89557

June 2007

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AWARD NO. DE-FG02-01ER45894

Personnel associated with project:

Katherine R. McCall, University of Nevada, Reno (Associate Professor)
Juergen Eckert, Los Alamos National Laboratory (Staff Scientist)
Mounira Boudjema, University of Nevada, Reno (PhD, May 2005; now a college physics instructor, Salala, Oman)
Patricia Gomez, University of Nevada, Reno (MS, December 2002; now providing software support, private industry, Walnut Creek, CA)
Jeremy Jensen, University of Nevada, Reno (MS, May 2005; now a high school science teacher, Albuquerque, NM)
Stacy Maddox, University of Nevada, Reno (MS, August 2002; now a high school science teacher, Reno, NV)

I. Project Description

The aim of this work was to use neutron scattering techniques to explore the dynamics and structure of water in rock samples. The dynamics of water in rock at low (residual) saturation are directly related to the transport properties of fluids within the host rock. The structure of water in rock may be related to the elastic behavior of the rock, which in many cases is nonlinear and hysteretic. Neutron scattering techniques allow us to study water in intact rock samples at both the molecular and microstructural scales. Our samples were Berea sandstone, Calico Hills and Prow Pass tuffs from Yucca Mountain, NV, and pure samples of the tuff constituents, specifically mordenite and clinoptilolite. We chose Berea sandstone because its macroscopic elastic behavior is known to be highly unusual, and the microscopic mechanisms producing this behavior are not understood. We chose Yucca Mountain tuff, because the fluid transport properties of the geologic structure at Yucca Mountain, Nevada could be relevant to the performance of a high level nuclear waste repository at that site.

Neutron scattering methods have a number of properties that are extremely useful for the study of earth materials. In contrast to X-rays, neutrons have very low absorption cross-sections for most elements so that entire bulk samples of considerable size can be “illuminated” by the neutron beam. Similarly, samples that are optically opaque can be readily investigated by inelastic neutron scattering techniques. Neutrons are equally sensitive to light atoms as to heavy atoms, and can, for example, readily distinguish between Al and Si, neighboring atoms in the periodic table that are difficult to tell apart by X-ray diffraction. Finally, neutrons are particularly sensitive to hydrogen and thus can be used to study the motions, both vibrational and diffusive, of H-containing molecules in rocks, most notably of course, water.

Our studies were primarily studies of guest molecules (in our case, water) in a host material (rock). We used three neutron scattering techniques: quasielastic neutron scattering (QNS), inelastic neutron scattering (INS), and neutron powder diffraction (NPD). We used QNS to measure the translational and rotational diffusional motion of water in rock; INS vibrational spectra allowed us to determine the nature of residual water in a sample (disassociated, chemisorbed, or physisorbed); and NPD measurements may allow us to determine the locations of residual water molecules (and the associated dynamic disorder), and thereby understand the binding of water molecules in our samples.

II. Results of Work

The nature of residual water and possible dynamics and transport properties of water molecules in various geologic host materials were studied using experimental techniques including quasielastic neutron scattering (QNS), inelastic neutron scattering (INS), neutron powder diffraction (NPD). Several students were involved in performing the experiments, completing the data analysis, and developing phenomenological models of water transport and behavior in confined geometries. Three students completed terminal MS degrees based on the work supported by this project and a fourth completed a PhD with partial support from this project. One refereed publication was published and three are in various stages of preparation. Manuscript publication has been slowed by an increased administrative load on the PI (department chair, Jan 2004 – June 2007).

INS data (Los Alamos National Laboratory) on Berea sandstone at residual water saturation, and QNS data (Argonne National Laboratory) on Berea sandstone at residual water saturation, Calico Hills tuff at residual, 5% and 10% water saturation, and Prow Pass tuff at residual saturation were analyzed. The temperature range for the experiments was 200 – 400 K. The results show that water dissociates in Berea sandstone at residual saturation and there is no discernable water motion over the entire temperature range. In contrast, the zeolitic components of the tuffs hold highly mobile water.

Calico Hills tuff is a devitrified tuff consisting primarily of zeolites (clinoptilolite, mordenite). Prow Pass tuff is composed primarily of quartz and feldspar. Data from the two samples was analyzed using a model for bulk water. Translational diffusion coefficients (self diffusion) and rotational activation energies were derived for the Calico Hills tuff. In the Prow Pass tuff translational diffusion coefficients were found, but no rotational activation energy. The residence time for translational diffusion was found to be noticeably longer than for bulk water for a given temperature.

For the Calico Hills sample at 5% saturation, the activation energy for rotational motion is 2.4 kJ/mol; at 10% saturation, the activation energy for rotational motion is 3.8 kJ/mol; and at room conditions, the activation energy for rotational motion is 5.4 kJ/mol. In contrast, the activation energy for rotational motion in bulk water is 7.7 kJ/mol. The difference may be rationalized by noting that a water molecule in the bulk would typically form four hydrogen bonds (two as donor, two as acceptor) with its neighbors, whereas a molecule on a surface is likely to participate in fewer H-bonds, and hence may be able to reorient more easily.

Translational motion was clearly evident in all tuff samples except the 5% saturated Calico Hills tuff. At room temperature, the diffusion coefficients are: 1.6×10^{-6} cm^2/s for Prow Pass tuff, 7.6×10^{-6} cm^2/s for the 10% saturated Calico Hills tuff, 15×10^{-6} cm^2/s for the room-dry Calico Hills tuff (compare to 23×10^{-6} cm^2/s for bulk water). The translational diffusion of water in tuff is slower than that in bulk water, but significantly faster than in many clays.

Further QNS measurements (Argonne National Laboratory) were performed to explore the diffusion of water in chlinoptilolite and mordenite – the main constituents of Yucca Mountain tuff – and to explore the saturation dependence of mobility of water in Berea sandstone. Measurements were made as a function of temperature and saturation to explore the saturation dependence of water behavior in Berea sandstone, and to determine the contribution of individual tuff components to the bulk tuff sample transport properties. The samples were powdered, vacuum-oven dried, and re-hydrated. Clinoptilolite-water samples were created by adding 3%, 6%, 9% and 12% water by weight to the vacuum-oven dried clinoptilolite. One mordenite-water sample with 6% water was created in a similar manner.

Analysis of the data on the zeolites indicates an increasing activation energy for rotational motion with increasing temperature, approaching the rotational activation energy for bulk water (7.73 kJ/mol). The rotational activation energy also increases as a function of water content in clinoptilolite. Mordenite at 6% water by weight has a rotational activation energy of 6.4 kJ/mol, while clinoptilolite at the same water content has an activation energy of 3.0 kJ/mol. This difference may be attributed to a difference in interaction potential – water in mordenite may interact preferentially with other water, rather than with the zeolite.

The rotational and translational diffusion coefficients increase with temperature for all of the zeolite samples. The clinoptilolite with 3%, 6%, and 9% water and the mordenite with 6% water have similar diffusion constants that seem to converge at high temperature. However, the clinoptilolite with 12% water has high temperature rotational and translational diffusion coefficients well above the other samples. These results and consideration of notes taken during sample preparation indicate that the 12% water by weight sample is saturated beyond the capacity of the zeolitic cages to hold water. Thus bulk water behavior begins to dominate the measured mobility. This bulk behavior is evident in the Berea sandstone samples at even lower saturations.

NPD measurements were made on six samples of clinoptilolite prepared in the following way. The H_2O in the clinoptilolite was exchanged for D_2O. The samples were then vacuum-oven dried and re-hydrated with specified D_2O and D_2O - H_2O mixtures. The data will be analyzed using pair distribution function analysis, to determine the water molecule locations within the zeolitic structure of clinoptilolite.

With a small amount of support from this project, a lattice Boltzmann model of fluid diffusive motion in confined geometries was developed. Direct application to neutron scattering measurements was not obvious, but the technique was found to be particularly amenable to modeling the results of nuclear magnetic resonance (NMR) measurements. NMR measurements have not been made on our samples due to the very low saturations studied. However, as the saturation increases, and thus the number of magnetic moments in the water that will contribute signal, NMR may become a complimentary technique for understanding the dynamics of water in rocks.

III. Manuscripts, Theses, Presentations, Beamtime proposals

Boudjema, M., K.R. McCall, and R. A. Guyer, Lattice Boltzmann simulations of fluid diffusive motion, Fall Meeting of the American Geophysical Union, San Francisco, CA, December 2001 (contributed poster).

Gomez, P., S. A. Maddox, K. R. McCall, and J. Eckert, Diffusion of water in Yucca Mountain tuffs, Fall Meeting of the American Geophysical Union, San Francisco, CA, December 2001 (contributed poster).

Maddox, S. A., P. Gomez, K. R. McCall, and J. Eckert, Water mobility in Calico Hills tuff measured by quasielastic neutron scattering, Geophys. Res. Lett. 29, 10.1029/2001GL014167 (2002).

McCall, K. R., Cold neutrons: the perfect way to study hot rocks, Physics Colloquium, San Diego State University, March 2002 (invited talk).

McCall, K. R., and J. Eckert, Water in constituents of Yucca Mountain tuff, LANSCE proposal for beamtime on the HIPPO diffractometer, Los Alamos National Laboratory, March 2002.

McCall, K. R., and J. Eckert, Diffusion of water in chlinoptilolite and mordenite – the main constituents of Yucca Mountain tuff, IPNS proposal for beamtime on the QENS

spectrometer, Argonne National Laboratory, April 2002.
McCall, K. R., Quasielastic neutron scattering and its application to earth materials, 7th International Workshop on Nonlinear Elastic Materials, Riva del Garda, Italy, August 2002 (invited presentation).
Maddox, S. A., A study of water mobility and dynamics in Calico Hills tuff using quasielastic neutron scattering, MS thesis, University of Nevada, Reno, August 2002.
Gomez, P., Diffusion of water in rock at low saturation, MS thesis, University of Nevada, Reno, December 2002.
McCall, K. R., J. Eckert, P. Gomez, and S. A. Maddox, Short time water mobility in tuff and constituents as a function of temperature and saturation, American Geophysical Union 2002 Fall Meeting, San Francisco, CA, December 2002 (contributed presentation).
McCall, K. R., Rocks in the Physics Lab, Physics Department Colloquium, Sonoma State University, February 2003 (invited presentation).
Boudjema, M., R.A. Guyer, and K.R. McCall, Lattice Boltzmann simulations of pulsed field gradient nuclear magnetic resonance, Fall Meeting of the American Geophysical Union, San Francisco, CA, December 2003 (contributed poster).
Boudjema, M., Lattice Boltzmann simulations of nuclear magnetic resonance phenomena in porous media, DOE workshop on Flow and Transport in Porous Materials, Gaithersburg, MD, September 2004.
McCall, K.R., Simulation of nuclear magnetic resonance in fluid filled pore spaces: a tool to understand complex geometries, Center for Engineering and Fluid Mechanics (CEAFM) Seminar, Johns Hopkins University, April 2005 (invited presentation).
Boudjema, M., Lattice Boltzmann studies of nuclear magnetic resonance in porous materials, PhD dissertation, University of Nevada, Reno, May 2005.
Jensen, J., The physical kinetics of water in Yucca Mountain zeolites via quasielastic neutron scattering, MS thesis, University of Nevada, Reno, May 2005.